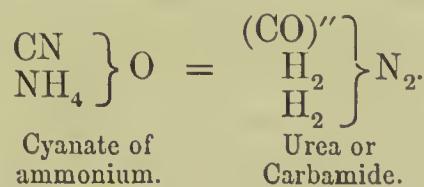


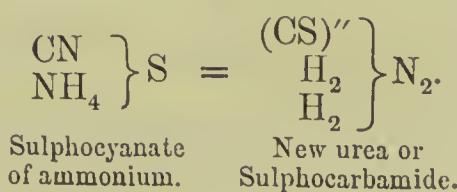
ON THE ISOLATION OF THE MISSING SULPHUR UREA.

By J. EMERSON REYNOLDS, Member of the Royal College of Physicians, Edinburgh; Keeper of the Minerals and Analyst to the Royal Dublin Society, &c.

WHEN an aqueous solution of cyanate of ammonium is simply evaporated to dryness, the salt is well known to undergo isomeric change, thereby yielding a body which is identical in properties with ordinary urea. The alteration which takes place in this beautiful process of Wöhler's, is usually represented in the following way by those chemists who regard urea as carbamide, or diammonia in which two equivalents of hydrogen are replaced by the diatomic radicle CO" or carbonyl :—



Cyanate and sulphocyanate of ammonium (sulphocyanide of ammonium) are well known to be salts of very similar constitution: hence the sulphocyanate should yield, on heating, a corresponding urea containing sulphur, thus :—



In the latter case the radicle (CS)" takes the place of the carbonyl in ordinary urea.

Owing to the great probability of effecting this change, the action of heat on the sulphocyanate of ammonium has been made the subject of special study by Baron Liebig, Professor Völkel, and other chemists, but with negative results, so far as the discovery of the sulphur urea was concerned. Still more recently Dr. Hofmann, in pursuing his valuable researches on the compound ammonias, has prepared, indirectly, a number of substitution-products of the sulphur urea, though this distinguished chemist did not succeed in isolating the body itself, and hence appears to have adopted the hypothesis that sulphocyanate of ammonium is the sulphur urea, but possessing a peculiarly pronounced saline constitution.*

The object of the present communication is to show that the sulphur urea can not only be prepared directly from the sulphocyanate of ammonium, but that it can be obtained in considerable quantities by a process precisely similar to that discovered by Wöhler for the artificial preparation of the ordinary or oxygen urea.

An attentive consideration of the points of similarity and of difference between cyanate and sulphocyanate of ammonium was sufficient to convince me that the greater stability of the latter salt must be the chief obstacle to the molecular rearrangement of its constituents. We are familiar with the fact that it is only necessary to evaporate an aqueous solution of cyanate of ammonium to dryness at a boiling temperature, in order to convert it completely into ordinary urea. The temperature of boiling water is, therefore, sufficient to induce isomeric change in the case of the cyanate. But the sulphocyanate is unaffected by similar treatment, and though unaltered at 100° C., under ordinary circumstances, it decomposes easily when heated alone at temperatures beyond 180° C. I was led by these considerations to examine closely the action of heat upon the sulphocyanate between the above ranges of temperature, and have been amply rewarded by the isolation of the missing sulphur urea.

The following is the mode of operating which experience has shown me to give the best result.

About 500 grammes of *well dried* sulphocyanate of ammonium

* Proceedings of Royal Society, vol. ix, p. 274.

should be placed in a flask of suitable size, a thermometer then introduced, and the whole heated *gradually** by means of an oil-bath to a temperature of about 170° C. for two hours. I may here mention, incidentally, that the fusing point of the perfectly dry salt was found on repeated trials with large quantities of material, to be 159° C., instead of 147° C., as stated in the books, the error in the latter case probably arising from the presence of moisture in the sample examined. When the temperature of the fused mass is carefully adjusted to nearly 170° C., but little ammonium sulphide is produced, and scarcely a trace of carbonic disulphide. When the mass has been kept in a state of fusion for a sufficient time, it is allowed to cool down, and when its temperature has reached 100° C., it is treated with its own weight of warm water (80° C.); when the whole has dissolved the solution is filtered at once through a small plug of cotton, for the purpose of separating a black substance, always formed in small quantity, and then left to crystallise.

After some hours the liquid yields an abundant crop of fine, long, silky crystals, which sometimes cling together in a remarkable manner. The crystals are now to be drained off from the mother-liquor, and pressed between folds of bibulous paper, and again crystallised from as small a quantity of boiling water as possible. The urea now crystallises in fine prisms, but not thicker than an ordinary sewing-needle. Owing to the pertinacity with which the sulphocyanate adheres to the new substance, several crystallisations are needed before it is obtained in a state of purity.

When perfectly dried *in vacuo* over sulphuric acid, the crystals were found to contain carbon, hydrogen, nitrogen, and sulphur. Owing to the presence of a large proportion of nitrogen and of sulphur in the compound, considerable difficulty was encountered in the determination of the carbon; fortunately, this is of rather less importance than usual, since the remaining constituents admit of direct estimation. After many trials, the following modification of the ordinary process was found to be best suited to the particular case. A combustion tube was employed in each instance between 85 and 90 centimetres long. A few centimetres of pure dry chromate of lead having been

* When the perfectly dry sulphocyanate is very quickly heated to beyond the fusing point, a body analogous to Linneman's sulphocyanic anhydride appears to be produced, as I have pointed out in another place.

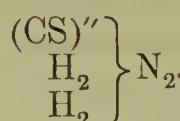
first introduced, an intimate mixture of the substance with warm chromate and then the rinsings of the mortar were added, so as to occupy about 30 centimetres; a layer of about 15 centimetres of plain chromate was now filled in, and a porous rod of copper occupied the anterior portion of the tube. The copper rod was obtained by rolling up *very closely*, fine copper gauze, so as to prepare a porous cylinder without any central tube. The rod so prepared was first heated in air, and then reduced in a current of hydrogen in the usual way, and when closely fitting to the combustion tube, was found to secure the complete reduction of the nitrogen oxides formed during the analysis. The combustion was conducted *very slowly*, and the temperature of the anterior layer of pure chromate of lead never allowed to get beyond a very low red heat.

The following are the results obtained:—

- I. ·2774 grm. of the carefully dried and pure substance gave ·13312 of water. Carbon determination a bad one.
- II. ·3923 grm. gave ·2295 of carbonic acid, and ·18242 water.
- III. ·259 grm. gave 1·524 grm. $(\text{NH}_4)_2\text{PtCl}_6$. And ·5 grm. gave, on treatment by Carius' method, 1·531 grm. $\text{Ba}''\text{SO}_4$.
- IV. ·5 grm. treated in the same way, gave 1·525 grm. $\text{Ba}''\text{SO}_4$.
The substance used in this estimation was crystallised from alcohol.

| | Calculated. | | Found. | | | |
|------------|-------------|---------|--------|--------|--------|--------|
| | | | I. | II. | III. | IV. |
| Carbon.... | 12 | 15·789 | — | 15·886 | — | — |
| Hydrogen | 4 | 5·263 | 5·330 | 5·166 | — | — |
| Nitrogen.. | 28 | 36·843 | — | — | 36·891 | — |
| Sulphur .. | 32 | 42·105 | — | — | 42·235 | 42·068 |
| | — | — | | | | |
| | 76 | 100·000 | | | | |

Analysis, then, leads well to the formula,—



It will be presently seen that this formula is corroborated by the analyses of several well marked compounds of the new urea.

The new substance occurs either in long fine crystals, or in very short thick prisms belonging, in either case, to the rhombic system. The crystals are non-deliquescent in moderately dry air, easily soluble in water and alcohol, and but slightly soluble in ether. The particular form in which the urea is obtained from either alcoholic or aqueous solution, is dependent to a great extent on the presence or absence of impurities. The solution froths slightly on agitation, has a neutral reaction, and rather bitter taste.

When the urea is heated with water in a sealed tube for some hours to 140° C., it is reconverted into sulphocyanate of ammonium, as evidenced by the intense red colour struck by the liquid on testing with a ferric salt. The urea itself when quite pure does not give a colour reaction with this test.

When digested with hydrate of potassium in a sealed tube for some hours, at a temperature of 100° C., the substance afforded ammonia, sulphhydrate, carbonate, and a little sulphocyanate of potassium. The essential decomposition which takes place in the presence of an alkali may be represented thus—



The decomposition with sulphuric or hydrochloric acid is precisely similar to the foregoing.

When boiled with dilute nitric acid, the sulphur is easily oxidized to sulphuric acid. Nitrites and hypochlorites liberate nitrogen from the urea. When treated with a large excess of permanganate of potassium and alkali, by Wanklyn and Gamgee's plan,* nitrogen is also set free, and the sulphur oxidized to sulphuric acid.

The fusing point of the new urea is 149° C. When gently heated upon platinum-foil, it fuses, and then volatilises without blackening or leaving a residue. When heated in a closed tube it fuses, then boils up, evolving sulphide of ammonium, carbonic disulphide, and ammonia (?); the mixture quickly blackens, but on continuing the heat, a yellow oil distils over, and a white mass is left in the tube. This residue strongly resembles Liebig's hydromellone.

When to a nearly saturated aqueous solution of the urea we add an excess of colourless nitric acid of specific gravity 1·25,

* Journ. Chem. Soc., vol. vi, p. 25.

avoiding any rise in temperature, we obtain a beautiful crystalline nitrate, sparingly soluble in the presence of nitric acid. A quantity of the salt was prepared and freed from nitric acid by repeated pressure between folds of blotting paper, until the crystals were almost completely dried; the final desiccation was then rapidly effected in a current of dry air,* and the substance analysed immediately, since it rapidly decomposes.

Having satisfied myself of the persistence of the molecule of the sulphur urea, I found that the proportion of it existing in its compounds could be accurately determined by estimating the sulphur present and calculating this into urea. This is the plan pursued in most of the analyses which follow:—

- I. 1·0 grm. of the pure nitrate gave 1·6515 grm. Ba^{''}SO₄, when treated by Carius' method. Very little heat is needed to effect the decomposition.
 II. 1·0 grm. gave 1·6603 Ba^{''}SO₄.

| | Calculated. | | Found. | |
|--|-------------|--------|--------|-------|
| | I. | II. | I. | II. |
| (CS) ^{''} H ₄ N ₂ | 76 | 54·67 | 54·22 | 54·39 |
| HNO ₃ | 63 | 45·33 | — | — |
| | 139 | 100·00 | | |

The results agree well with the formula.



I have not succeeded in obtaining a hydrochlorate of this urea.

1·0039 grms. of the dry substance, when subjected to a current of dry hydrochloric acid gas for two hours, at first without and afterwards with heat, did not undergo any apparent change, and increased in weight to the extent of 1·0103 grm.

I have not hitherto been able to prepare an oxalate.

Gold Compound.—If to a saturated aqueous solution of the pure sulphur urea, a nearly neutral solution of trichloride of gold be added very gradually, a yellow colour is soon developed

* I attempted to dry a quantity, of about 6 grammes, of the nitrate *in vacuo* over sulphuric acid, but after some hours drying, the whole suddenly decomposed with a slight explosion.

in the liquid. On the addition of each drop of the gold solution, a reddish precipitate appears, which quickly redissolves. The point to be reached is that at which fresh gold solution ceases to be decolorised *quickly*. The liquid, on slow evaporation, yields beautiful, pearly, monoclinic crystals, which, on recrystallisation, are obtained pure.

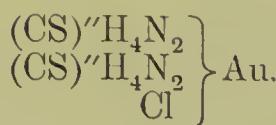
The crystals were found to contain the new urea, chlorine, and gold.

I. ·2387 gave ·12195 grm. of gold, on cautious ignition after previous treatment with nitric acid.

II. ·6596 grm., treated with nitric acid, the liquid diluted, and precipitated by chloride of barium; ·797 grm. Ba"SO₄, obtained = 16·66 per cent. of sulphur. The filtrate was then evaporated nearly to dryness, with addition of sulphuric and hydrochloric acids; the solution, after sufficient dilution, was freed from the new precipitate of sulphate of barium, and the gold thrown down from the filtrate by ferrous sulphate. ·33655 grm. was obtained.

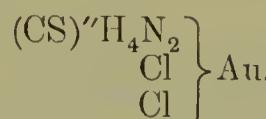
| | Calculated. | | Found. | |
|---------------------------------------|-------------|---------|--------|----------------------|
| | I. | II. | I. | II. |
| Au..... | 196·0 | 51·134 | 51·09 | 51·02 |
| Cl..... | 35·5 | 9·236 | — | 9·42 (by difference) |
| 2(CS" H ₄ N ₂) | 152·0 | 39·630 | — | 39·56 |
| | — | — | — | — |
| | 383·5 | 100·000 | | |

I have therefore assigned to this salt the singular formula—



and we shall presently find that the composition of one of the platinum compounds proves the truth of the view which I now take of the constitution of this beautiful salt. All the ureas with which we are acquainted possess more or less decided basic characters, and, under certain conditions, very feeble acid functions also; but in the case of the new substance we have, I believe, the first instance of an urea which manifests very strongly marked acid functions, and correspondingly feeble basic characters.

In preparing the salt just described, it will be observed that the urea must be kept in excess, but when the gold solution preponderates, a reddish-yellow precipitate is produced, which decomposes so rapidly that it was found impossible to obtain it in a condition suitable for analysis; however, when we consider the constitution of the stable body already described, there appears to be some reason to believe that the red compound would turn out to be



if it could be separated in a state of sufficient purity for examination.

Platinum-compounds.—With platinum several compounds can be obtained. One of these bodies is highly characteristic of the new urea, and this I have studied with care.

When a solution of tetrachloride of platinum, containing as little free acid as possible is added to a slight excess of the aqueous solution of the sulphur urea, a bulky, highly crystalline, red precipitate is produced. The appearance of the precipitate is remarkable, and under the microscope the compound is well characterised by the peculiar plumose appearance of the long prismatic crystals. The precipitate when produced as described, must be quickly washed, first with water and then with alcohol. After pressing between folds of bibulous paper it must be rapidly dried at a temperature not exceeding 80° C. This platinum compound decomposes easily if left moist for some time, but keeps very well when thoroughly dry and free from tetrachloride of platinum.

In the present instance I did not consider it safe to determine the sulphur and platinum only, but sought for direct evidence of the permanence of the molecule of the sulphur urea by the estimation of the nitrogen and chlorine in addition.

Different preparations of the same salt were used in the following analyses:

I. ·5265 grm. of a very carefully prepared and quickly dried sample gave ·2268 grm. Pt.

·4035 grm. gave when oxidized with nitric acid ·4 grm.
 $\text{Ba}''\text{SO}_4$.

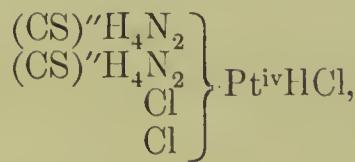
II. ·2729 grm. of another specimen gave, on ignition, ·1172 grm. Pt.

III. ·5374 grm. was cautiously fused with crystallised hydrate of barium, and small fragments of nitrate of ammonium added until no further action was produced; the mass was then digested with water, an excess of dilute nitric acid added, the solution filtered, and the chlorine determined in the filtrate; ·4909 grm. of AgCl was obtained. A slight loss was unavoidable.

·5045 grm. after ignition with soda-lime gave ·9872 $(\text{NH}_4)_2\text{PtCl}_6$.

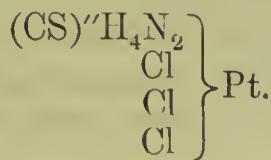
| | Calculated. | | Found. | |
|----------------------|-------------|--------|--------|-------|
| | | I. | II. | III. |
| Pt..... | 197·0 | 43·15 | 43·18 | 42·94 |
| Cl ₃ | 106·5 | 23·33 | — | 22·62 |
| S ₂ | 64·0 | 14·03 | 13·95 | — |
| N ₄ | 56·0 | 12·26 | — | 12·22 |
| C ₂ | 24·0 | 5·26 | — | — |
| H ₉ | 9·0 | 1·97 | — | — |
| | 456·5 | 100·00 | | |

The analysis leads well to the formula



thus according in constitution with the equally well defined gold salt.

If instead of adding a nearly neutral solution of tetrachloride of platinum to an excess of the sulphur urea in aqueous solution, we add the latter to an excess of platinic chloride containing free hydrochloric acid, we get but little if any precipitate till after the lapse of some time; then a dirty brown precipitate gradually deposits, which is freed from excess of platinic chloride with difficulty. A specimen so prepared, washed until incipient decomposition was observed, and then dried, gave 52·38 per cent. of metallic platinum. The formula



requires 51.97 per cent. of platinum. However, though there is considerable probability of the truth of the above formula for the dirty brown platinum salt, I only wish to be understood as suggesting it here, since this substance and two other platinum salts which the urea is capable of affording, require further investigation. I can only add that I have not succeeded in obtaining any platinum compound corresponding to the ordinary double salt of the metal.

Silver Compound.—When a solution of nitrate of silver is added to one of the urea, and the mixture heated, the precipitate first formed dissolves, but sulphide of silver quickly separates in flakes unless some free nitric acid be present. When the clear hot solution containing free acid is allowed to cool, a mass of coherent silky needles makes its appearance and must be collected, drained well, and re-crystallised from water containing free nitric acid. When well dried by pressure, the desiccation must be rapidly completed in a current of dry air at ordinary temperatures. Even when adopting these precautions, it is impossible to prevent slight decomposition, since the presence of a small quantity of nitric acid appears to be essential to the stability of the compound.

The following are the analytical results:—

I. .572 grm. of the salt gave .5701 grm. Ba^{II}SO₄. And .867 grm. gave .5391 grm. AgCl.
II. .4879 grm. gave .3003 grm. AgCl.

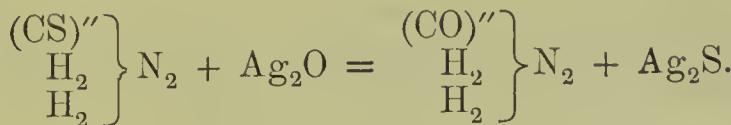
| | Calculated. | | Found. | |
|---|-------------|--------|--------|-------|
| | I. | II. | I. | II. |
| 2(CS) ^{II} H ₄ N ₂ | 152 | 33.33 | 32.63 | — |
| 2Ag | 216 | 47.36 | 46.80 | 46.33 |
| O | 16 | 19.31 | — | — |
| 4H ₂ O | 72 | — | — | — |
| | 456 | 100.00 | | |

These figures agree tolerably well with the formula.



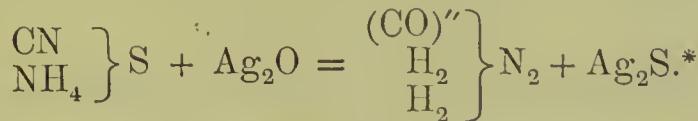
When the compound is gently heated in a tube, water is evolved, and, on increasing the heat, a slight explosion occurs with formation of sulphide of silver and the production of a crystalline sublimate.

Owing to the facility with which this urea yields up its sulphur to silver or other metal when the liquid is neutral or alkaline, I attempted the conversion of the new substance into the ordinary or oxygen urea in accordance with the following equation :



For this purpose quantities of the sulphur urea and of hydrate of silver, in accordance with the foregoing equation, were gently heated together with a little water for half an hour. The solution was then filtered from the sulphide of silver which had formed. The liquid left on evaporation a rather deliquescent crystalline residue, which was dissolved in alcohol; on evaporation of the alcoholic solution, fine prismatic needles were obtained. When the crystals were dissolved in water, and Liebig's test solution of mercuric nitrate added, a white precipitate was immediately obtained, which disappeared on running in solution of chloride of sodium. A sparingly soluble oxalate was also prepared and a nitrate. From the foregoing observations I conclude that the sulphur urea described in this paper, when treated with silver oxide, yields ordinary urea and sulphide of silver.

There is a process for preparing carbamide, which is but little known, and consists in heating a solution of sulphocyanate of ammonium with oxide of silver, the equation generally supposed to express the change which ensues being as follows :



We have now good reason to believe that this is but an incomplete expression of the change, since there can be little doubt that, in the first stage of the reaction, sulphur urea is produced, and this is subsequently attacked by the silver oxide as already pointed out.

The physiological interest attached to the question of the conversion of the new urea into the well known oxygen compound, is so considerable that I intend making it the subject of special enquiry.

* Naquet's Chemistry, translated by Cortis, p. 708.

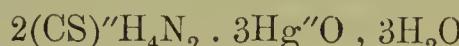
Mercurial Salts.—Several compounds of the sulphur urea with mercuric oxide and its salts appear to exist; of these, however, I will at present notice but one.

When nearly neutral solution of mercuric nitrate (Liebig's test) was added to a somewhat dilute solution of the sulphur urea, a precipitate was not immediately formed, but a crystalline body was ultimately thrown down, which, when washed and dried, gave the following results:

- I. 1·1894 grm. of the compound when treated with chlorate of potassium and hydrochloric acid, gave 1·5282 grm. of Ba"SO₄; and 1·9376 grm. gave on ignition in a tube in the usual way, with pure lime, 1·6627 grm. Hg.
- II. 1·718 grm. gave 1·50425 grm. Hg.

| | Calculated. | | Found. | |
|---|-------------|--------|--------|------|
| | I. | II. | I. | II. |
| 2((CS)"H ₄ N ₂)..... | 152 | 17·79 | 15·46 | — |
| 3Hg"O..... | 648 | 75·88 | 76·35 | 76·2 |
| 3H ₂ O | 54 | 6·33 | — | — |
| | 854 | 100·00 | | |

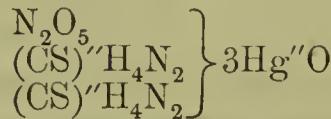
It would thus appear that the formula



is the correct one for this body, as I have reason to believe that this substance loses urea and water on prolonged washing, and becomes



When the mercuric nitrate is largely in excess the compound



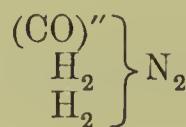
appears to be formed.* But I do not pursue the subject further here, since the composition of some of these metallic salts requires special investigation, and sufficient proof has now been given of the accuracy of the formula which I have obtained for the sulphur urea itself.

* The construction adopted in the text is employed for the purpose of exhibiting the relation of the compound to one of the basic mercuric nitrates which the well-known researches of Sir Robert Kane have made us acquainted with.

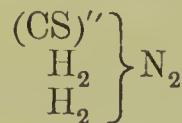
General Observations.—It will be easily perceived from the foregoing statements that the new urea described in this memoir must now take the place hitherto assigned to the sulphocyanate of ammonium, the latter salt falling back into its true position as the strict chemical analogue of cyanate of ammonium.

This change of idea is rendered necessary since some chemists—finding that Liebig and Völkel failed in converting the sulphocyanate of ammonium into the sulphur urea—have regarded the latter body and the sulphocyanate as identical, not only in centesimal composition, but in constitution likewise.

If we regard the oxygen urea as carbamide



we must consider the sulphur urea as sulphocarbamide—



and we then have the new body as the primary of the following compound ureas, which have been discovered from time to time by Dr. Hofmann in his fine researches on the polyammonias.

| | |
|---|---|
| Sulphocarbamide | $\left. \begin{matrix} (\text{CS})'' \\ \text{H}_2 \\ \text{H}_2 \end{matrix} \right\} \text{N}_2$ |
| Allyl-sulphocarbamide | $\left. \begin{matrix} (\text{CS})'' \\ \text{C}_3\text{H}_5 \\ \text{H}_3 \end{matrix} \right\} \text{N}_2$ |
| Allyl-naphtyl-sulphocarbamide | $\left. \begin{matrix} (\text{CS})'' \\ \text{C}_3\text{H}_5 \\ \text{C}_{10}\text{H}_7 \\ \text{H}_2 \end{matrix} \right\} \text{N}_2$ |
| Ethyl-allyl-sulphocarbamide | $\left. \begin{matrix} (\text{CS})'' \\ \text{C}_2\text{H}_5 \\ \text{C}_3\text{H}_5 \\ \text{H}_2 \end{matrix} \right\} \text{N}_2$ |
| Phenyl-sulphocarbamide | $\left. \begin{matrix} (\text{CS})'' \\ \text{C}_6\text{H}_5 \\ \text{H}_3 \end{matrix} \right\} \text{N}_2$ |

| | | |
|------------------------------------|---|--|
| Diphenyl-sulphocarbamide | $(CS)''$ C_6H_5 C_6H_5 H_2 | $\left. \begin{matrix} N_2 \\ N_2 \end{matrix} \right\}$ |
| Phenyl-allyl-sulphocarbamide | $(CS)''$ C_6H_5 C_3H_5 H_2 | |

We may also add to the list of bodies which may be regarded as derivatives of the new urea, the complex amide obtained by Hofmann in acting upon sulphocyanate of allyl with triethyl-phosphine—

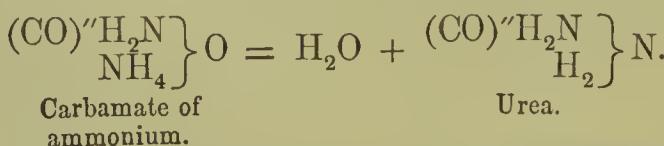
| | | |
|--|--|---|
| Allyl-triethyl-sulpho-carbophosphamide | $(CS)''$ C_3H_5 C_2H_5 C_2H_5 C_2H_5 | $\left. \begin{matrix} N \\ P. \end{matrix} \right\}$ |
| | | |

And the analogous compound :

| | | |
|---|--|---|
| Phenyl-triethyl-sulpho-carbophosphamide | $(CS)''$ C_6H_5 C_2H_5 C_2H_5 C_2H_5 | $\left. \begin{matrix} N \\ P. \end{matrix} \right\}$ |
| | | |

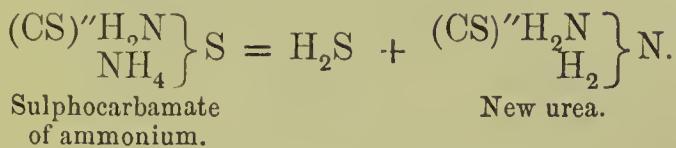
I may observe here that many interesting questions connected with the constitution of the above mentioned group of compound ureas now appear to admit of satisfactory solution, since we are acquainted with the primary of the series.

I cannot conclude this paper without venturing to predict the formation of the sulphur urea by the action of heat on sulphocarbamate of ammonium. Basaroff* has recently succeeded in realising the suggestion of Professor Kolbe, that carbamate of ammonium would afford ordinary urea by simple dehydration, since the latter chemist does not regard urea as carbamide, but rather as the amide of carbamic acid. If we express the change effected by heating carbamate of ammonium in accordance with Kolbe's view, thus—



* Journal of Chem. Soc., vol. vi, p. 194.

then sulphocarbamate of ammonium should yield the sulphur urea in a similar way.



I have little doubt that this idea will be realized if sufficient care be taken in conducting the experiment.

Laboratory, Royal Dublin Society,
December 3rd, 1868.

